



Synthesis and characterization of one-dimensional titanate structure

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Abstract

One-dimensional titania structures were synthesized through a simple hydrothermal process in a highly alkaline conditions. The aim of this work was to elucidate the effect of time on the formation of 1D titanates as well on its structural characteristics (morphology, phase composition, surface area). Apart from that, the effect of heat treatment conditions on the stability of titanate based 1D samples has been investigated. The results have revealed that it is possible to form one-dimensional titanates already after 1 hour of hydrothermal synthesis. Although the composition of titanates is still under debate, the results probably correspond to the layered sodium titanates. The 1D prepared structures show a remarkable stability during heating, remaining the basic morphology and composition even up to 700°C.

Keywords: one-dimensional titanates, hydrothermal synthesis, thermal stability

I. Introduction

In the past decades, titania as semiconducting material has attracted a great scientific interest due to its wide range of applications in many fields such as catalysis and electronics, namely in manufacturing different sensor and optical devices [1,2]. Properties and applications of titania depend on its type of crystalline phase, dimension of structure units, morphology, composition, etc. [3,4]. Discovery of carbon nanotubes and their exceptional properties related to the one dimensional structure (1D) has introduced a new challenge in research and tailoring one-dimensional structure of titania. One-dimensional nanostructured materials (nanotubes, nanorods, nanowires, nanobelts) considering their specific structural characteristics, primarily their high aspect ratio and large specific surface area, show fascinating properties compared to the bulk counterparts [5]. Among these materials, 1D titanate (titania) nanomaterials have received a great deal of attention because of their technological importance in solar cells, photoelectrochemical conversion, as photocatalysts in the degradation of pollutant in environmental protection,

as absorbents, catalytic support, gas sensors [6–8]. Type and structural characteristics of 1D materials, as well as their properties are strongly determined on the processing method and conditions of preparation. In general, there are three main approaches for the preparation of these materials: template methods [9], anodic oxidation [10,11], and wet chemical methods [12–14]. Recently, the synthesis of titania 1D structures fabricated by a hydrothermal method proposed by Kasuga *et al* has received considerable attention because of its low cost and simplicity.

Besides the growing interest in obtaining 1D titanates, the formation mechanism and phase of these materials are still subjects of debate [15]. According to the literature, different crystal structures and compositions have been suggested, such as trititanate ($\text{H}_2\text{Ti}_3\text{O}_7$), tetratitanate $\text{H}_2\text{Ti}_4\text{O}_9 \cdot \text{H}_2\text{O}$, lepidocronite titanates $\text{H}_x\text{Ti}_{2-x/4}\text{O}_4$, $\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$, $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ and TiO_2 anatase [13–16]. In addition, some authors have concluded that 1D structures were formed by rolling of single layers peeled from crystal plates possibly due to hydrogen deficiency in surface [13]. On the other hand, some researchers explain this mechanism by wrapping of multilayer nanosheets [16]. However, a completely distinct mechanism of nanotube formation has been proposed in some publications [17,18]. Au-

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thors have suggested that the rollup theory is only valid when local concentration fluctuations generate extreme conditions (temperature, pH and reaction time) at the surface of nanoparticles. It was claimed that local concentration fluctuations which have appeared on the crystallite of starting material under hydrothermal conditions, initiate the formation of nanoloops from the starting material, which then become seeds for an oriented crystal growth process leading to titanate nanotubes. The shape of the cross-section is determined by the curvature of the seeding nanoloop. Since these are flexible ensembles only a few nanometers in length and diameter, they can give rise to spiral, onion, or even multiple-spiral nanotube cross-sections. The thermal stability of 1D nanostructure is of critical importance for their implementation as building blocks in nanoscale electronic and photonic devices, but there are limited studies considering this subject [19]. It is important to note that the products obtained after thermal decomposition of the 1D titanate can provide some crucial evidence necessary to elucidate their original crystal structure.

The main subject of this work is to investigate the early stage of titanate formation, but also the effect of heat treatment conditions on their stability is discussed.

II. Experimental

One dimensional nanostructured titania based materials were synthesized by hydrothermal processing in highly alkaline conditions. Commercial titania powder (Degussa P-25) was used as a starting material. Following the hydrothermal procedure, TiO_2 powder was dispersed in an aqueous solution of 10 M NaOH, and ultrasonically treated for an hour. After the treatment in ultrasonic bath the specimen was transferred into a sealed vessel (volume 100 ml) with 84% autoclave filling fraction [20]. The hydrothermal reaction was carried out in an oil bath at 150°C for dif-

ferent periods of time up to 10 hours. As-synthesized powders were separated from the slurry and washed a number of times with distilled water and ethanol until neutral pH was reached. Finally, formed titania based structures were dried at 120°C for one day. In order to investigate the thermal stability, obtained titanates were heated at different temperatures up to 900°C. The samples were noted as Tm-x, where x stands for the time of hydrothermal reaction (1, 3, 6 and 10 hours).

As-synthesized powders were characterized by X-ray diffraction, XRD (Siemens D500 instrument using Ni-filtered Cu-K α radiation of wavelength 1.5418 Å), Fourier-transform infrared spectroscopy, FT-IR (Nicolet-Nexus 670 FT-IR), low temperature nitrogen adsorption, BET (Quantachrom Autosorb-3B instrument), scanning electron microscopy, SEM (JEOL JSM 6460LV) with energy-dispersive X-ray spectroscopy, EDS (Oxford INCA EDS system) and transmission electron microscopy, TEM (Hitachi H9000-NA).

III. Results and Discussion

The typical FT-IR spectrum for commercial powder P25 (mixture of anatase and rutile) is given in the left upper corner of the Fig.1, and shows the characteristic bands in the range 450–700 cm^{-1} related to the different types of Ti-O-Ti vibrations. However, according to the spectra of the as-prepared titanates (Fig. 1), the shape of these bands was changed, implying the structure modification and formation of one-dimensional titanate structure. In addition, new band appeared at around 900 cm^{-1} which corresponds to the vibration of Ti-O nonbridging oxygen bonds, and probably the formation of Ti-O-Na bonds. This band is typical for one-dimensional structures [4], but the small intensity could be explained by the very low concentrations of Na ions (due to extensive ion exchange with H^+ during washing). The shape and intensity of the observed bands are changing with

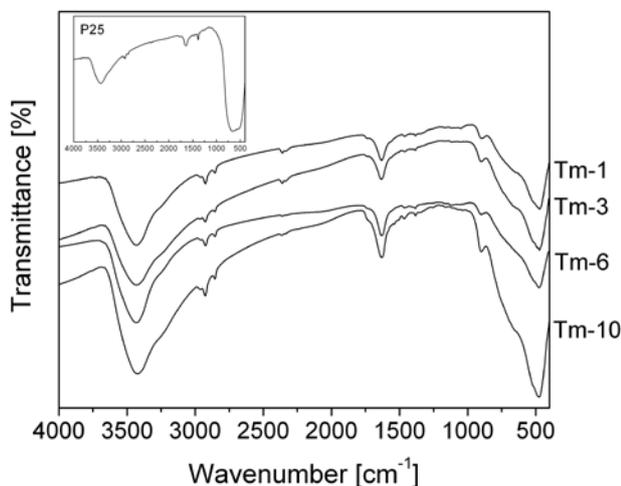


Figure 1. FT-IR spectra of as-prepared 1D titanates and starting powder P25 (in the left upper corner)

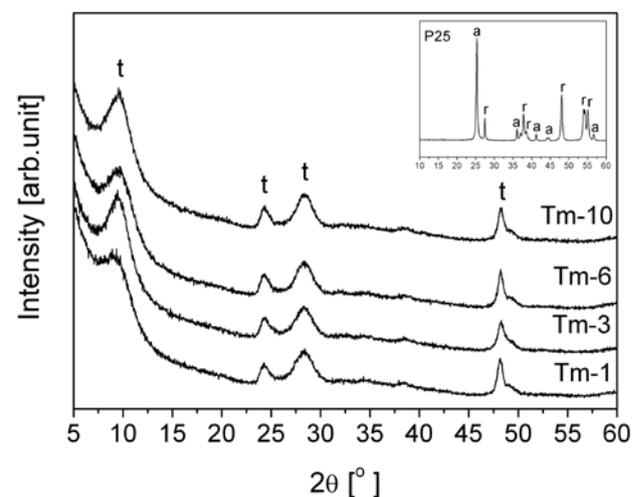


Figure 2. XRD patterns of as-prepared 1D titanates and starting powder P25 (t - $\text{Na}_2\text{Ti}_3\text{O}_7$, a - anatase, r - rutile)

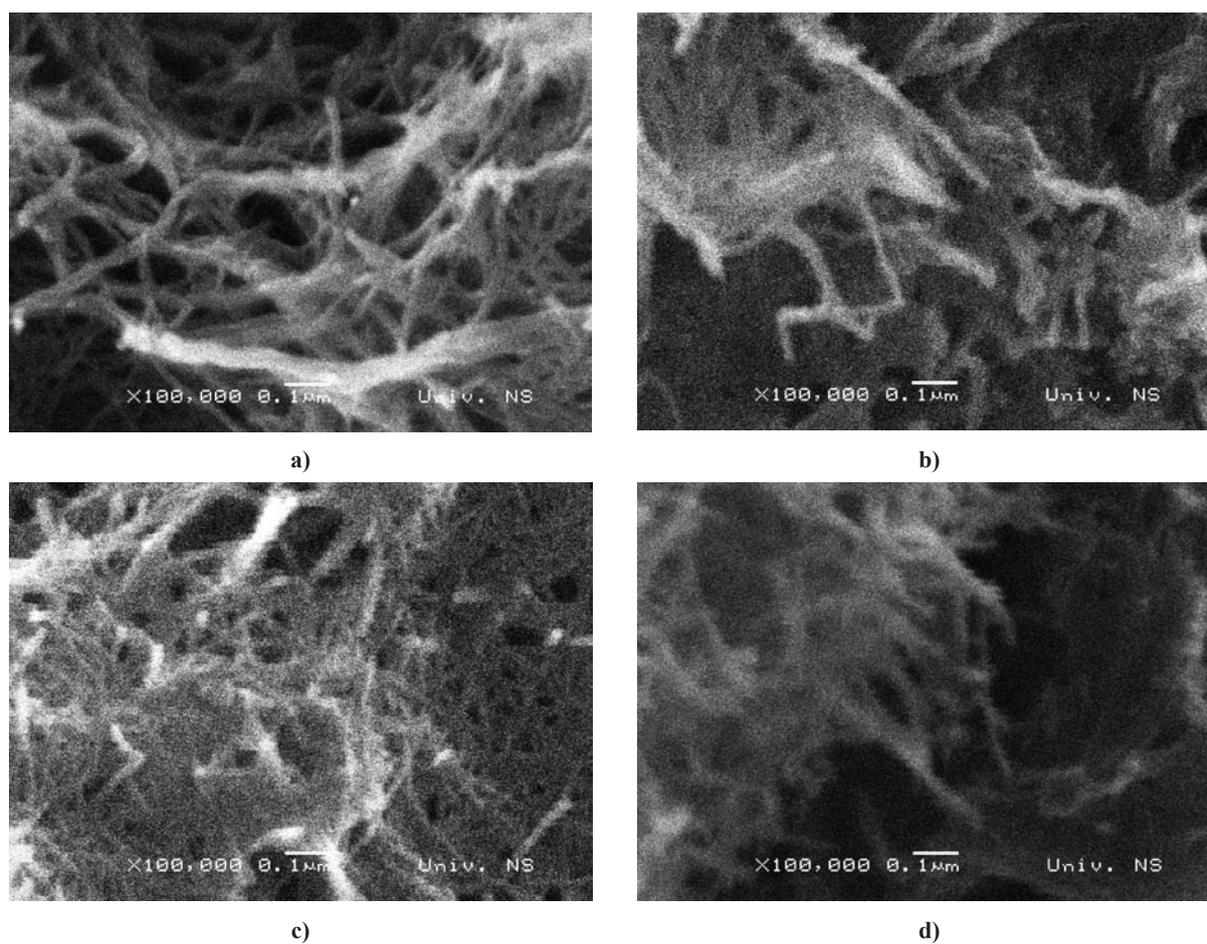


Figure 3. SEM images of as-prepared 1D titanates: a) Tm-1, b) Tm-3, c) Tm-6 and d) Tm-10

the time of hydrothermal reaction. A broad and intense band located around 3400 cm^{-1} can be ascribed to OH-stretching vibrations. The presence of this peak implies the existence of hydroxyl groups and large amount of water molecules in the surface and interlayer space. Vibration around 1650 cm^{-1} also confirmed the presence of water and can be assigned to H-O-H bending vibrations of water.

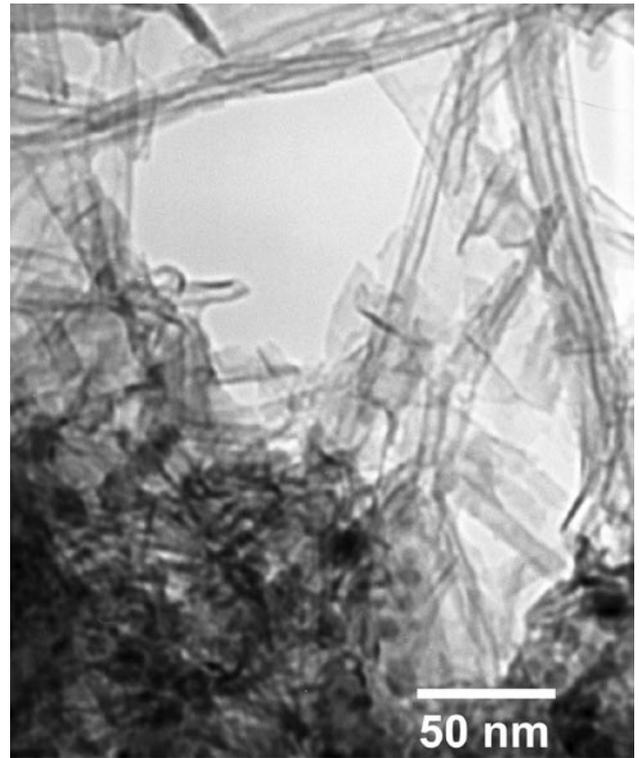
Obtained XRD results confirmed the FT-IR findings as can be observed according to patterns presented in Fig. 2. In order to follow the structure changes in the powder after hydrothermal reaction, the XRD pattern of the starting material is given in the corner. It is important to mention that 1D titanate structures are present already after one hour of hydrothermal synthesis, which is an unusually short time, never documented in the literature according to our knowledge. The XRD patterns showed mainly four diffraction peaks at $2\theta \sim 9.5, 24, 28$ and 48° characteristic for $\text{Na}_2\text{Ti}_3\text{O}_7$ type of titanates (JCPDS 31-1329), in accordance with the literature [2,16,21]. These peaks could be ascribed to the interlayer spacing typical for one-dimensional titanate structure [2,4,13–16]. The intensity of the peak around 9.5° is increasing with the reaction time, indicating the rise in crystallinity.

SEM analysis of as-prepared powders confirmed that one dimensional titanate structure is obtained already after one hour of hydrothermal reaction, Fig. 3. Morphology of these forms depends on reaction time and in order to investigate it more precisely and try to obtain information on the formation mechanism, TEM analyses were conducted and the results depicted in Fig. 4. According to TEM images, nanosheets and also nanotubes are observed. Some of these nanotubes are only partially scrolled, so it could be assumed that 1D structures are most probably formed by delamination and rolling-up of precursor nanosheets into scrolled nanotubes. Of course, to state this possible way of formation, further investigations are necessary. It is important to notice that particle-like morphology of the precursor, does not exist any more, implying that the rate of hydrothermal reaction is very high in the early stage of one-dimensional structure formation. In addition, the specific surface area of these structures is remarkably increased (even up to $450\text{ m}^2/\text{g}$) in respect to the starting powder, P25 (about $80\text{ m}^2/\text{g}$).

Composition of obtained 1D titanates, suggested considering the XRD results, is confirmed by EDS analyses, Fig. 5. There is a visible peak of sodium ion, which shows that the formed titanates contain Na^+ , probably setting in interlayering space [15].



a)



b)

Figure 4. TEM images of as-prepared 1D titanates: a) Tm-1, b) Tm-10

Fig. 6 shows the XRD patterns of Tm-1 sample calcined at different temperatures for one hour. The pattern of the samples heat treated at 500°C is very similar to the as-prepared 1D titanates, except that the intensity of diffraction peak near $2\theta \sim 10^\circ$ was shifted towards higher angle value indicating a decrease in the interlayer distance for this plane. This contraction of layers may be due to the release of water molecules adsorbed and present in interlayer spacing. The remaining diffraction peaks are only slightly modified suggesting the maintenance of the crystallographic and morphological structure up to 500°C. The observed phase is stable even af-

ter calcination at 700°C, although other titanate phases are starting to appear and all can be ascribed to sodium titanates ($\text{Na}_2\text{Ti}_3\text{O}_7$ - JCPDS 31-1329; $\text{Na}_2\text{Ti}_6\text{O}_{13}$ - JCPDS 37-0951). As expected the calcined forms show better crystallinity in respect to as-prepared titanates. Similar results were obtained for the other samples.

The change in shape and morphology of obtained titanates in relation to the calcination temperature was followed by SEM. Fig. 7 shows the SEM micrographs of titanates heated at 900°C. It can be noticed that during heat treatment the one-dimensional morphology remained, but with different aspect ratios in compari-

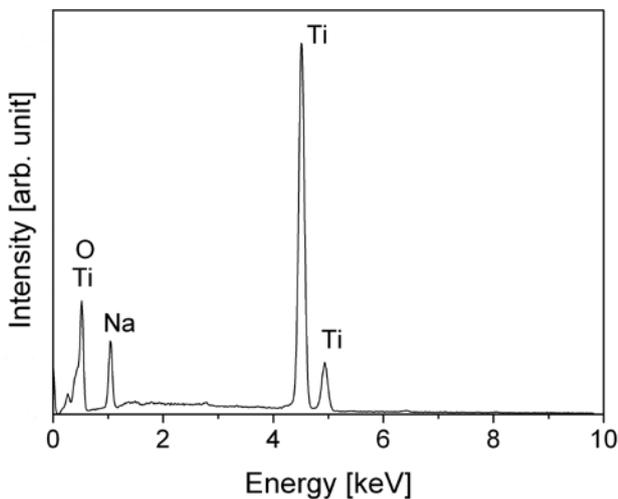


Figure 5. EDS spectrum of as-prepared Tm-10 sample

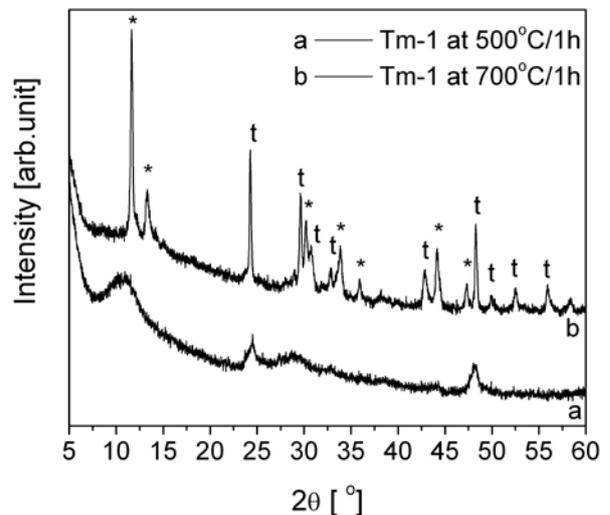


Figure 6. XRD patterns of Tm-1 sample after calcination at 500°C/1h and 700°C/1h (t - $\text{Na}_2\text{Ti}_3\text{O}_7$, * - $\text{Na}_2\text{Ti}_6\text{O}_{13}$)

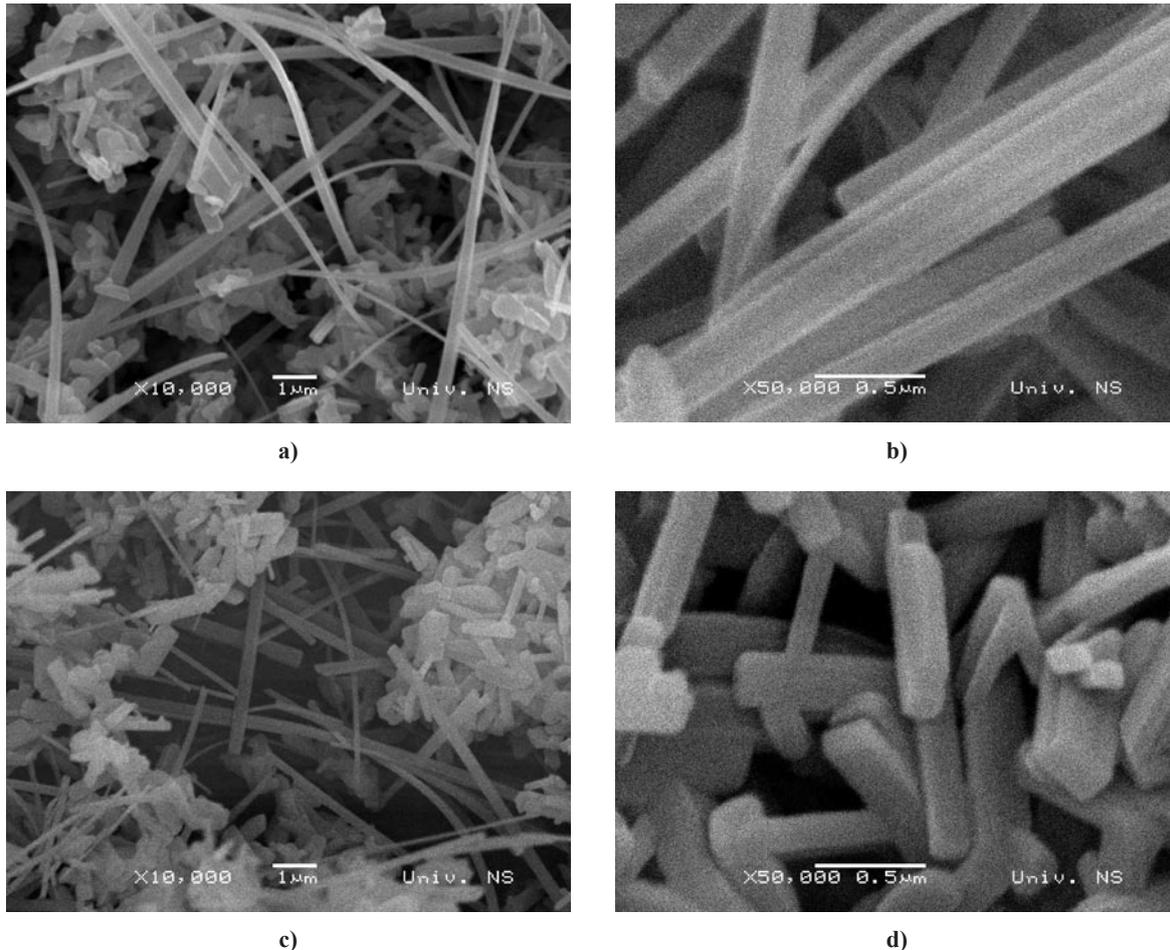


Figure 7. SEM images of titanate samples heated at 900°C: a) Tm-1, b) Tm-3, c) Tm-6 and d) Tm-10

son to as-prepared samples. This process induces a variety of 1D structures like whiskers, belts, rods, fibers etc. Temperature affected the process of densification and crystal growth, which resulted in coarsening of 1D structures.

VI. Conclusions

One-dimensional titanate structures were successfully obtained directly from a highly alkaline solution of titania powder following a hydrothermal process already after one hour of synthesis. We have shown that as-prepared titanates contain sodium with a composition probably based on sodium trititanates. The study of thermal effect has shown that obtained one-dimensional titanates maintain the same composition under heating up to 500°C. Heat treatment at higher temperatures induces the appearance of the other titanate phases, but they preserve the morphology, which is typical for one-dimensional structures.

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References

1. E.I. Kapinus, T.A. Khalyavka, V.V. Shimanovskaya, T.I. Viktorova, V.V. Strelko, “Photocatalytic activity of spectro-pure titanium dioxide: Effects of crystalline structure, specific surface area and sorption properties”, *Inter. J. Photoen.*, **05** (2003) 159.
2. J. Yu, M. Zhou, “Effects of calcinations temperature on microstructures and photocatalytic activity of titanate nanotube films prepared by an EPD method”, *Nanotechnol.*, **19** (2008) 045606 (6pp).
3. H. Liu, L. Gao, “Preparation and properties of nanocrystalline α -Fe₂O₃-sensitized TiO₂ nanosheets as a visible light photocatalyst”, *J. Am. Ceram. Soc.*, **89** [1] (2006) 370–373.
4. J.A. Toledo-Antonio, S. Capula, M.A. Cortes-Jacome, C. Angeles-Chavez, E. Lopez-Salinas, G. Ferrat, J. Navarrete, J. Escobar, “Low-temperature FTIR study of CO adsorption on titania nanotubes”, *J. Phys. Chem. C*, **111** (2007) 10799–10805.
5. W. Wang, H. Lin, J. Li, N. Wang, “Formation of titania nanoarrays by hydrothermal reaction and their application in photovoltaic cells”, *J. Am. Ceram. Soc.*, **91** [2] (2008) 628–631.
6. F. Dong, W. Zhao, Z. Wu, “Characterization and photocatalytic activities of C, N and S co-doped TiO₂ with 1D nanostructure prepared by the nano-confinement effect”, *Nanotechnol.*, **19** (2008) 365607 (10pp).

7. S. Yuan, Q. Sheng, J. Zhang, F. Chen, M. Anpo, Q. Zhang, "Synthesis of La³⁺ doped mesoporous titania with highly crystallized walls", *Micropor. Mesopor. Mater.*, **79** (2005) 93–99.
8. M. Sacerdoti, M.C. Dalconi, M.C. Carotta, B. Cavicchi, M. Ferroni, S. Colonna, M.L. Di Vonad, "XAS investigation of tantalum and niobium in nanostructured TiO₂ anatase", *J. Solid State Chem.*, **177** (2004) 1781–1788.
9. S. Zhang, C. Liu, Y. Liu, Z. Zhang, G. Li, "Fabrication of micrometer-scale anatase-phase TiO₂ congeries assembled with hollow spheres", *J. Am. Ceram. Soc.*, **91** [6] (2008) 2067–2070.
10. M. 'Ou Li, X. Xiao, R. Liu, "Synthesis and bioactivity of highly ordered TiO₂ nanotube arrays", *Appl. Surf. Sci.*, **255** [2] (2008) 365–367.
11. Y. Yin, Z. Jin, F. Hou, X. Wang, "Synthesis and morphology of TiO₂ nanotube arrays by anodic oxidation using modified glucerol-based electrolytes", *J. Am. Ceram. Soc.*, **90** [8] (2007) 2384–2389.
12. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, "Titania nanotubes prepared by chemical processing", *Adv. Mater.*, **11** [15] (1999) 1307–1311.
13. C.-C. Tsai, H. Teng, "Structural features of nanotubes synthesized from NaOH treatment on TiO₂ with different post-treatments", *Chem. Mater.*, **18** (2006) 367–373.
14. H.-H. Ou, S.-L. Lo, "Review of titania nanotubes synthesized via the hydrothermal treatment: Fabrication, modification and application", *Sep. Purif. Technol.*, **58** (2007) 179–191.
15. S. Xu Chun, E. Yang, Z. Yi Fan, "Synthesis of M_xH_y-Ti₃O₇ nanotubes by simple ion-exchanged process and their adsorption property", *Chin. Sci. Bull.*, **52** [18] (2007) 2491–2495.
16. M. Qamar, C.R. Yoon, H.J. Oh, N.H. Lee, K. Park, D.H. Kim, K.S. Lee, W.J. Lee, S.J. Kim, "Preparation and photocatalytic activity of nanotubes obtained from titanium dioxide", *Catalysis Today*, **131** (2008) 3–14.
17. A. Kukovecz, M. Hodos, E. Horvth, G. Radnczi, Z. Konya, I. Kiricsi, "Oriented crystal growth model explains the formation of titania nanotubes", *J. Phys. Chem. B*, **109** [38] (2005) 17781–17783.
18. E. Horvth, A. Kukovecz, Y. Konya, I. Kiricsi, "Hydrothermal conversion of self-assembled titanate nanotubes into nanowires in a revolving autoclave", *Chem. Mater.*, **19** [4] (2007) 927–931.
19. Y. Yang, X. Wang, L. Li, "Crystallization and phase transition of titanium oxide nanotube arrays", *J. Am. Ceram. Soc.*, **91** [2] (2008) 632–635.
20. B. Poudel, W.Z. Wang, C. Dames, J.Y. Huang, S. Kunwar, D.Z. Wang, D. Banerjee, G. Chen, Z.F. Ren, "Formation of crystallized titania nanotubes and their transformation into nanowires", *Nanotechnol.*, **16** (2005) 1935.
21. A.-L. Sauvet, S. Baliteau, C. Lopez, P. Fabry, "Synthesis and characterization of sodium titanates Na₂Ti₃O₇ and Na₂Ti₆O₁₃", *J. Solid State Chem.*, **177** (2004) 4508–4515.